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(71) Applicant (for all designated States except US): IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB).			
(72) Inventor; and (75) Inventor/Applicant (for US only): JENKINS, Stephen, Derek [GB/GB]; 71 The Paddock, Stokesley, Middlesbrough, Cleveland TS9 5PN (GB).			
(74) Agents: THOMAS, Ieuan et al.; ICI Chemicals & Polymers Limited, Intellectual Property Dept., P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE (GB).		Published With international search report.	
(54) Title: BARRIER POLYESTER			
(57) Abstract A film or hollow shaped article prepared from a low PETN copolymer resin wherein the resin has at least one of (a) an oxygen permeability of less than 2000 cc- μ m/m ² -day-atmos at 30 °C; (b) a density of greater than 1.3400 g/cm ³ ; or an area of the peak in tan δ centred at T β of less than 75 % of that for PET. Such articles have improved gas barrier performance, particularly impermeability to oxygen.			

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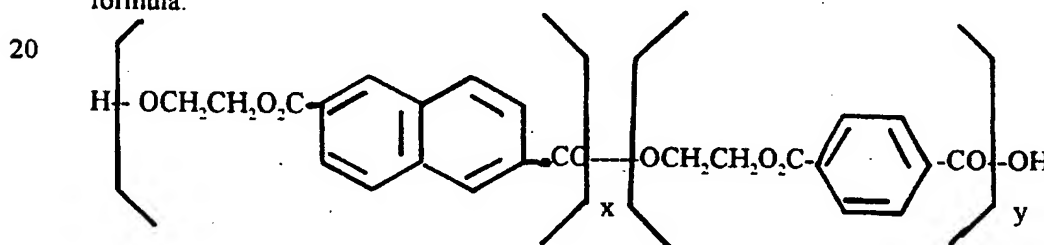
Barrier Polyester

The present invention relates to modified polyethylene terephthalate film and hollow shaped articles, particularly bottles and containers, more particularly bottles and containers having enhanced gas-barrier properties, and the preparation of such film and articles.

As the market for polyester packaging materials, particularly for containers for a variety of foods and beverages, has developed, the need for materials having a better gas barrier performance than polyethylene terephthalate (PET) has been identified. It has been recognised that those needs could often be met by polyethylene 2,6-naphthalenedicarboxylate (PEN) resin. However, there are significant market segments where the cost of PEN resin cannot be justified.

In US 4,609,721 there are described modified PET resins the melt strength of which has been increased by the incorporation therein of a minor amount of, for example, ethylene 2,6-naphthalenedicarboxylate repeat units. Polyester copolymers comprising ethylene terephthalate and ethylene 2,6-naphthalenedicarboxylate repeat units are hereinafter referred to for convenience as "PETN" copolymer resins.

Random copolymers comprising ethylene terephthalate and ethylene 2,6-naphthalenedicarboxylate repeat units may be represented by the following structural formula:



25 where x = mole fraction of naphthalate-based units and y = mole fraction of terephthalate-based units, based upon total moles of carboxylate units.

Hereinafter, a suffix will be appended to PETN which will indicate the mole fraction of naphthalate-based units, based upon total moles of carboxylate units, in the PETN copolymer. For example, a PETN copolymer comprising 15 mole fraction of naphthalate-based units and 85 mole fraction of terephthalate-based units will be represented by PETN15.

The preparation of films and bottles prepared from PETN copolymer resins has been described in Japanese Patent Publication No 49-22945.

In US 4,340,721 there are described PETN copolymer resins which contain 1.5-7.5 mole% of ethylene 2,6-naphthalenedicarboxylate repeat units and which are
5 suitable for the manufacture of bottles of reduced residual acetaldehyde content.

In US 4,474,918 it has been suggested that films or sheets prepared from modified PETN containing up to 50 mole % 2,6-naphthalenedicarboxylic acid and 1-30 mole % of a defined naphthalenediol or bisphenol have greatly reduced oxygen permeability.

10 In US 4,574,148 it has been disclosed that containers prepared from certain polyester copolymer resins prepared from a diol having up to 8 carbon atoms, a certain sulphur-containing diacid and 2,6-naphthalenedicarboxylic acid have improved resistance to gas permeability.

Clear blends of PET resin and PEN resin containing a so-called compatibilising polyester for providing clarity therein have been described in US 5,006,613. Those blends
15 preferably contain about 35-60 wt% PET, about 30-60 wt % PEN and about 5-15 wt% of the compatibilising polyester. The compatibilising polyester comprises about 10-20 mole % ethylene terephthalate repeat units and about 80-90 mole % ethylene 2,6-naphthalenedicarboxylate repeat units, eg PETN85. However, containers prepared
20 from such blends are often characterised by an undesirable yellowness.

In US 5,102,705 there are disclosed bottles made from highly stretched PEN resin. Such bottles reputedly have *inter alia* good gas barrier properties and superior heat resistance. It suggests that up to 40 mole% of the ethylene 2,6-naphthalenedicarboxylate repeat units in the PEN may be replaced by repeat units derived from an alternative
25 aromatic dicarboxylic acid, eg ethylene terephthalate.

In US 4,574,148 there are disclosed copolymers of PEN derived from a sulphur-containing di-acid, eg [thiobis(p-phenyleneoxy)]diacetic acid, which can be formed into bottles reputedly having good gas-barrier properties.

In Japanese Publication No. 3-122116 there is disclosed the preparation of bottles
30 by the injection moulding of certain PETN copolymer resins wherein 3-25 mole% of the repeat units are provided by ethylene 2,6-naphthalenedicarboxylate.

We have now found surprisingly that low PETN copolymer resins, preferably PETN12 and PETN16, particularly at a high draw ratio as hereinafter defined, ie at least 11, and preferably at a draw ratio between 11 and 15, drawn at a temperature between $T_{\alpha} + 15^{\circ}\text{C}$ and $T_{\alpha} + 30^{\circ}\text{C}$ of the low PETN copolymer resin and at a rate of at least 425% strain/sec, and preferably 425-850% strain/sec, have dramatically improved gas barrier performance, eg an oxygen permeability of less than 2000 cc- $\mu\text{m}/\text{m}^2\text{-day-atmos}$ at 30°C and often less than 1000 or even 600 cc- $\mu\text{m}/\text{m}^2\text{-day-atmos}$ at 30°C.

By "low PETN copolymer resins" we mean PETN copolymer resins containing between 8 mole% and 20 mole% ethylene 2,6-naphthalenedicarboxylate repeating units, ie PETN8 - PETN20.

By T_{α} we mean the glass transition temperature of the amorphous polymer as determined using a Perkin-Elmer DSC7 differential scanning calorimeter, at a test temperature range of 50-300°C, ramped at 20°C/min.

According to a first aspect of the present invention there is provided a film or a hollow shaped article, preferably a container or bottle, prepared from a low PETN copolymer resin which has an oxygen permeability of less than 2000 cc- $\mu\text{m}/\text{m}^2\text{-day-atmos}$ at 30°C, preferably less than 1000 cc- $\mu\text{m}/\text{m}^2\text{-day-atmos}$ at 30°C and more preferably less than 600 cc- $\mu\text{m}/\text{m}^2\text{-day-atmos}$ at 30°C.

The hollow shaped article may be made by blow moulding, preferably by injection stretch-blow moulding.

Without detriment to the present invention, we believe that the improved gas barrier performance of these low PETN copolymer resins drawn at high draw areas is based on a mechanism in the orientation process resulting in a significant and unexpected reduction in the diffusion of oxygen therethrough. We believe that this reduction arises from a combination of both the lower free volume and an inhibition of molecular motion at temperatures below T_{α} of these low PETN copolymer resins drawn at high draw areas.

By free volume we mean the volume of the polymer not directly associated with the molecular chains.

Determination of relative free volume can be obtained from density column experiments. Free volume can be determined directly by Positron Annihilation Lifetime

measurements (PAL), which gives a measure of the relative number of free volume cavities and their size.

The reduction in free volume of the low PETN copolymer resin may be a direct result of improved orientation of the polymer chains arising from the high draw area
5 under the temperature and strain rate conditions used in the preparation thereof.

By molecular motion below T_{α} we mean segmental motion of the polymer chains, typically characterised by a secondary transition at a temperature T_{β} .

Determination of changes in the secondary transition of these materials can be obtained using, for example, a Polymer Laboratories Dynamic Mechanical Thermal
10 Analyser with a tensile head attachment, at a test frequency of 10 Hz and temperature range of -120 to 150°C, ramped at 2°C/min. In particular the relative area of the peak in $\tan \delta$ centred at T_{β} can be estimated.

By $\tan \delta$ we mean the ratio of the loss modulus to the storage modulus under the test conditions used.

15 Without detriment to the present invention, we believe that the naphthalate content of the low PETN copolymer resin may be sufficient to inhibit molecular motion below T_{α} .

According to a further aspect of the present invention there is provided a film or a hollow shaped article, preferably a container or bottle, prepared from a low PETN
20 copolymer resin wherein the film or the walls of the article comprise a resin which has a density of greater than 1.3400 g/cm³, preferably greater than 1.3500 g/cm³, and/or in which the area of the peak in $\tan \delta$ centred at T_{β} is less than 75% of that for PET.

The film or hollow shaped article according to the further aspect of the present invention is preferably prepared by biaxially drawing a sheet or preform of low PETN
25 copolymer resin under tension to a draw ratio of at least 11.

According to a yet further aspect of the present invention there is provided a process for the preparation of a film according to the first or further aspects of the present invention which process comprises the step of biaxially drawing a sheet of low
30 PETN copolymer resin under tension to a draw ratio of at least 11, preferably between 11 and 15.

The sheet of low PETN copolymer resin which is biaxially drawn in the process according to the yet further aspect of the present invention is preferably prepared by casting a sheet of low PETN copolymer resin from the melt. However, we do not exclude the possibility that the sheet may be prepared by alternative processes known in the art.

By "draw ratio" we mean the ratio of the surface area of the biaxially drawn film prepared in the process according to the yet further aspect of the present invention to the surface area of the sheet used in the process.

According to a yet further aspect of the present invention there is provided a process for the preparation of a hollow shaped article according to the first or further aspects of the present invention which process comprises the Steps of:

- A) forming a preform by injection moulding a low PETN copolymer resin; and
- B) biaxially stretching the preform by blowing to a blow-up ratio of at least 11, preferably between 11 and 15.

By "blow-up ratio" we mean the ratio of the surface area of the article produced in Step B at the mid-wall thickness thereof to the surface area of the preform at the mid-wall thickness thereof.

In the processes according to the yet further aspects of the present invention, biaxial drawing of the film and biaxial stretching of the preform are carried out:

- (a) at a temperature between $T_{\alpha} + 15^{\circ}\text{C}$ and $T_{\alpha} + 30^{\circ}\text{C}$ of the low PETN copolymer resin ; and
- (b) at a rate of at least 425 % strain/second, preferably at a rate between 425 and 850 % strain/second, and more preferably between 500 and 666 % strain/second, in orthogonal directions.

In Step B of the process claimed in Claim 12 of the claims appended hereto biaxial stretching of the hot preform is carried out by (a) the stretching of the preform in the axial direction (along the preform length) by a mechanically driven rod, typically a metal rod, inserted through the open neck of the preform with (b) accompanying inflation of the preform in the hoop direction by pressurised gas delivered through the neck of the preform. The so-called stretch blow moulding process is essentially simultaneous biaxial orientation. This process is widely used commercially using appropriate moulds for the generation of hollow shaped articles.

We do not exclude the possibility that the low PETN copolymer resin of which the film or hollow shaped articles according to the first and further aspects of the present invention are comprised may be a blend, although this is not preferred. For example, blends of PET and PEN, or PET and PETN, or PETN and PETN, or PETN and PEN in appropriate ratios, eg 0-20wt% PEN and 100-80wt% PET, could be held for long residence times in the extruder of an injection moulding machine above the melt temperatures of the blend components, to allow sufficient transesterification to occur to produce products having the properties of low PETN copolymer resins.

The present invention is further illustrated by reference to the following
 10 Examples.

In the Examples:

- a) oxygen permeability of the film was determined using an OXTRAN 10-50 machine;
- b) intrinsic viscosity [IV(MV)] was determined from melt viscosity which was measured by melt flow of a sample (3.8g) through a 0.51mm diameter die under an applied pressure of 34.47-206.84 kPa nitrogen gas at a temperature of 295°C for resin of IV(MV) > 0.7dl/g and a temperature of 284°C for resin of IV(MV) < 0.7dl/g; and
- c) cast films were biaxially drawn on a film stretching apparatus (ex T M Long Co., New Jersey, USA) at $T_{\alpha} + 15^{\circ}\text{C}$, $T_{\alpha} + 20^{\circ}\text{C}$ or $T_{\alpha} + 30^{\circ}\text{C}$ and 425% strain/sec to the draw areas indicated in the Tables.

20 It will be appreciated that there is an empirical relationship between intrinsic viscosity measured on polymer melt, IV(MV) (in Pa.s), and the widely used intrinsic viscosity measured on a solution of polymer in o-chloro-phenol, IV(SOL) (in dl/g). This relationship is given by the following equations:
 at 284°C

$$25 \quad \text{IV(SOL)} = \text{Exp}[(\log_{10} \text{IV(MV)} - 3.487) \times 0.401567]$$

and at 295°C

$$\text{IV(SOL)} = \text{Exp}[(\log_{10} \text{IV(MV)} - 3.2481) \times 0.460518]$$

Examples 1-3

These Examples illustrate PETN copolymer resins for use in film or in hollow shaped articles according to the present invention.

Ester interchange was effected by heating ethylene glycol (42.0 litres; 2.09 moles), dimethyl terephthalate (61.60kg; 88 mole %) and dimethyl

2,6-naphthalenedicarboxylate (10.56kg; 12 mole%) (in the preparation of PETN12) or ethylene glycol (42.0 litres; 2.09 moles), dimethyl terephthalate (58.80kg; 84 mole%) and dimethyl 2,6-naphthalenedicarboxylate (14.09k g; 16 mole%) (in the preparation of PETN16) respectively in an autoclave at 0.39 MPa and 220-240°C for 2.5 hours using a proprietary combination of catalysts. Polycondensation of the ester interchange product was carried out under vacuum at 20.0Pa at 285°C for 1.1 hours. The product from the polycondensation reaction was found to have an IV(MV) of 0.65 dl/g. Solid state polymerisation of the polycondensation product was carried out on a fluidised bed at a gas flow rate of 60m³/hr, measured using nitrogen at atmospheric pressure, until a copolymer resin of IV(MV) 0.80 dl/g was obtained. In the solid state polymerisation step the temperature profile in the preparation of PETN12 and PETN16 was typically: ambient to 80°C over 30 mins; 80 to 120°C over 2 hours; 120 to (200-230)°C over 1 hour; maintained at 200-230°C for 6-10 hours and allowed to cool.

Amorphous sheets of thickness (230 ±20)µm were prepared from the low PETN resin copolymers by casting molten resin at 285°C onto a cooled rotating casting drum. The amorphous sheets were drawn at a draw temperature of T_α+20°C to draw areas greater than 11.

In Comparative Tests CT1 - CT8, the oxygen permeabilities of drawn films of PETN95, PETN92, PETN88, PETN84, PETN8, and PETN3 copolymer resins and PEN and PET resins, all of IV(MV) 0.80dl/g, prepared and drawn to draw areas greater than 11 by the aforementioned method, were likewise determined.

The results are shown in Table 1.

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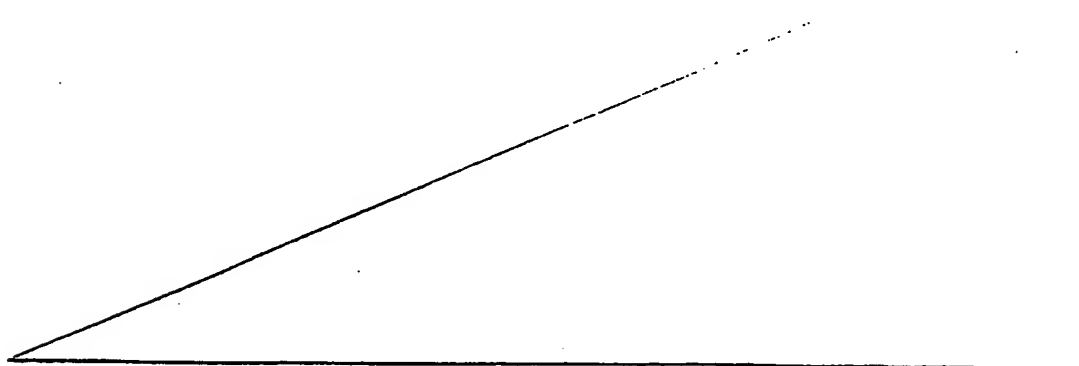


TABLE 1

EXAMPLE NO.	RESIN	T α (°C)	DRAW AREA	O ₂ PERMEABILITY cc- μ m/m ² -day-atmos at 30°C
1	PETN16	89.14	13.6	422 \pm 50 to 1790 \pm 100*
2	PETN12	88.46	13	464 \pm 50 to 1951 \pm 100*
3	PETN16	89.14	11.6	477 \pm 50 to 1826 \pm 100*
CT1	PEN	123.83	12	125 \pm 50 to 512 \pm 100*
CT2	PETN95	122.35	13.2	608 \pm 100
CT3	PETN92	122.08	12.7	614 \pm 100
CT4	PETN88	123.08	14.1	670 \pm 100
CT5	PETN84	118.54	12.6	615 \pm 100
CT6	PETN8	78.22	11.63	2438 \pm 100
CT7	PETN3	82.93	11.8	2835 \pm 100
CT8	PET	80.8	11.2	2454 \pm 100

T α : Determined by DSC (50-300°C; 20°C/min ramp)

CT: indicates a Comparative Test

*: indicates the range of experimental values recorded

In Comparative Tests CT9 and CT10, samples of the cast sheets of PETN16 and PETN12 prepared in Examples 1 and 2 were drawn to draw areas less than 11 at a draw temperature of T α + 20°C and the oxygen permeabilities of the drawn films were likewise determined.

In Comparative Tests CT11 - CT17, cast sheets of PEN, PETN95, PETN92, PETN88, PETN84, PETN8, PETN3 and PET resins, all of IV(MV) 0.80dl/g, prepared by the method described above were drawn to draw areas less than 11 at a draw temperature of T α + 20°C and the oxygen permeabilities of the drawn films were determined.

The results of CT9 - CT17 are shown in Table 2.

TABLE 2

EXAMPLE NO.	RESIN	T α (°C)	DRAW AREA	O ₂ -PERMEABILITY cc- μ m/m ² -day-atmos at 30°C
5 CT9	PETN16	89.14	8.2	2300±195
CT10	PETN12	88.46	8.3	2516±155
CT11	PEN	123.83	8.3	647±100
CT12	PETN95	122.35	8.4	775±100
10 CT13	PETN92	122.08	8.3	705±124?
CT14	PETN84	118.54	9.5	718±100
CT15	PETN8	78.22	8.1	2763±100
CT16	PETN3	82.93	8.2	3059±100
15 CT17	PET	80.8	8	2586±176

T α : determined by DSC (20-300°C; 20°C/min ramp)

CT: indicates a Comparative Test

From Table 1, results at high draw ratio, and Table 2, results at draw ratio less than 11, it can be seen that:

- 20 a) the oxygen permeability of PETN16 at high draw ratio is less than 600 cc- μ m/m²-day-atmos at 30°C (Examples 1 & 3) and is lower than the oxygen permeability of PETN16 at a draw ratio less than 11 (CT9);
- b) the oxygen permeability of PETN12 at high draw ratio is less than 600 cc- μ m/m²-day-atmos at 30°C (Example 2) and is lower than the oxygen permeability of
- 25 PETN12 at a draw ratio less than 11 (CT10);
- c) the oxygen permeabilities of PET, PETN3, PETN8, PETN95, PETN92, PETN88, and PETN84 at high draw ratio are not less than 2000 cc- μ m/m²-day-atmos at 30°C; and
- d) the oxygen permeabilities of PET, PETN3, PETN8, PETN95, PETN92 and PETN84 at high draw ratio are not significantly lower than the oxygen permeabilities thereof at a
- 30 draw ratio less than 11.

In Comparative Tests CT18 - CT20 cast sheets of PETN16 and PETN12 resins, both of IV(MV) 0.80dl/g, prepared by the method described above were drawn to draw areas greater than 11 but at draw temperatures outside the temperature range defined in Claim 14 and the oxygen permeabilities of the drawn films were determined.

5 The results are shown in Table 3.

TABLE 3

EXAMPLE NO.	RESIN	T α (°C)	DRAW TEMP. (°C)	DRAW AREA	O ₂ -PERMEABILITY cc- μ m/m ² -day-atmos. at 30°C
10 CT18	PETN16	89.14	T α +15	11.2	2106 \pm 100
CT19	PETN12	88.46	T α +15	14	2179 \pm 87
CT20	PETN16	89.14	T α +30	14	2005 \pm 100

T α : determined by DSC (20-300°C; 20°C/min ramp)

15 CT: indicates a Comparative Test

From Table 3 it can be seen that at draw temperatures of T α +15°C and T α +30°C the oxygen permeabilities of PETN16 and PETN12 are not less than 2000 cc- μ m/m²-day-atmos at 30°C.

Examples 4 -5

20 These Examples illustrate films of low PETN copolymer resins as claimed in Claim 3.

Cast sheets of PETN12, PETN16, PET and PEN, all of IV(MV) 0.80dl/g, were biaxially drawn at T α +20 °C and 425% strain to the draw ratios indicated in Table 4 and the Tan δ (β max), Tan δ (α max) and Tan δ area of β peak were determined.

25 The results are shown in Table 4 from which it can be seen that the areas of the peak in tan δ centred at T β is less than 75% of that for PET.

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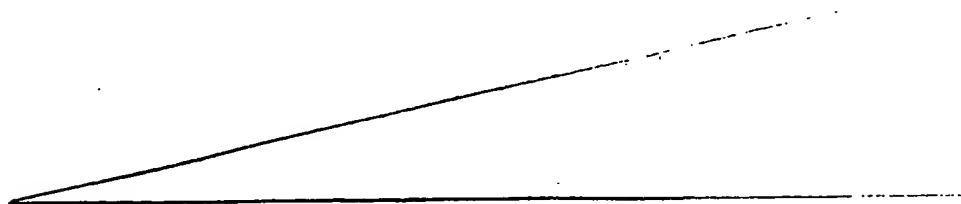


TABLE 4

Example No.	Resin	Draw Ratio	Tan δ β max. ($^{\circ}\text{C}$)	Tan δ Area of β peak (Relative Units)	% PET peak
4	PETN16	13.6	-46	1100	46
5	PETN12	11.4	-45	1700	71
CT21	PET	11	-44	2400	100
CT22	PEN	12	-49	260	11

CT: Comparative test.

%PET peak: % of area of the peak in Tan δ centred at T_{β} for PET.

Examples 6 -9

These Examples illustrate films of low PETN copolymer resins as claimed in Claim 2.

The low PETN copolymer resins in Examples 6-9 and the resins in the Comparative Tests CT23 - CT27 were all drawn at $T_{\alpha} + 20^{\circ}\text{C}$ and 425% strain rate to the draw ratios indicated in Table 5.

The results are shown in Table 5 from which it can be seen that, at draw ratios greater 11.0, PETN12 and PETN16, had densities greater than $1.3500 \text{ (g/cm}^3\text{)}$ and PETN84, PETN88, PETN92, PETN95 and PEN had densities less than $1.3500 \text{ (g/cm}^3\text{)}$.

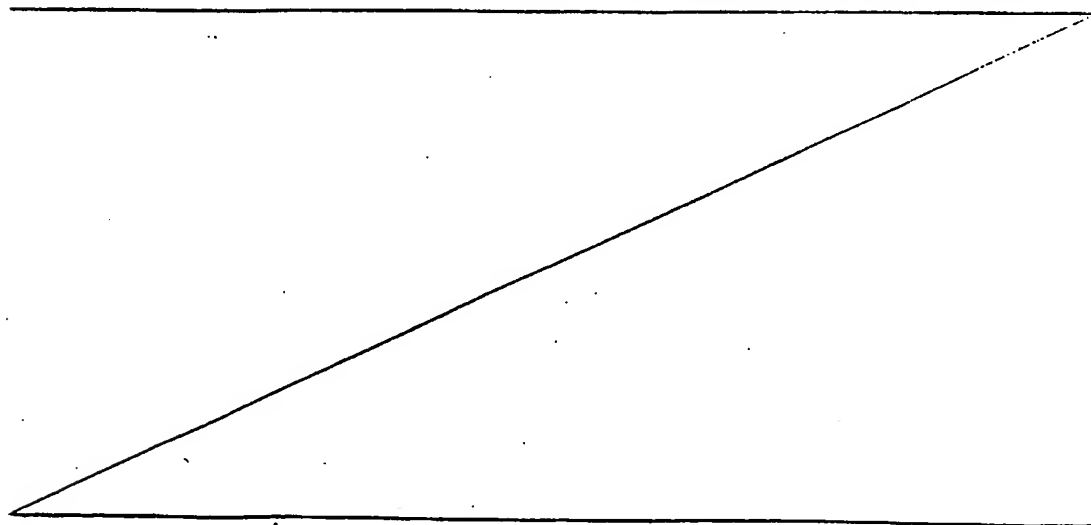


TABLE 5

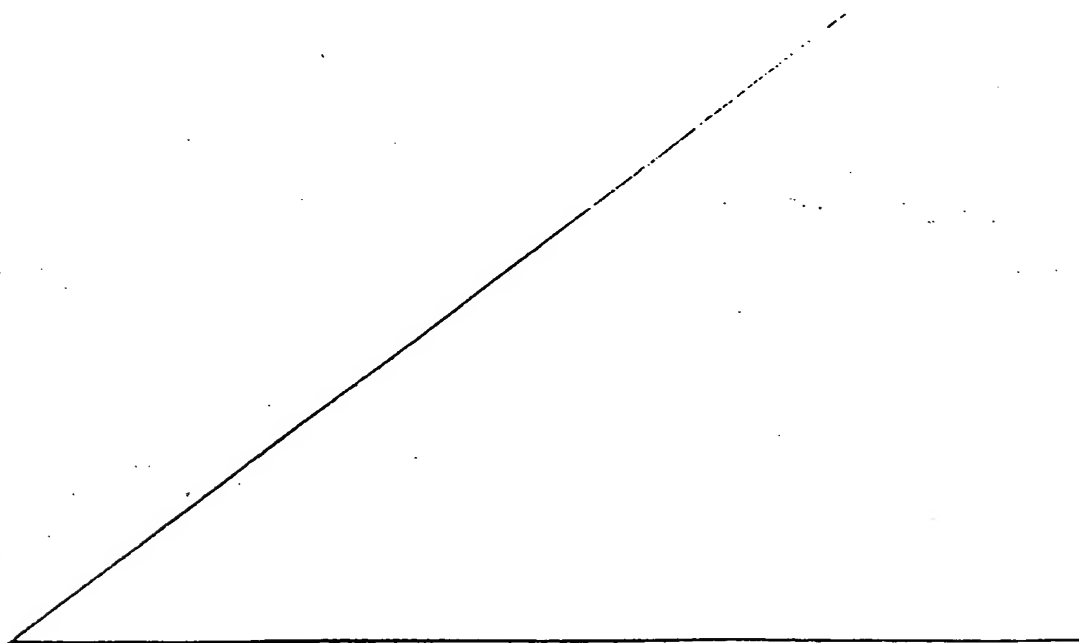
Example No.	Resin	Draw Ratio	Density (g/cm ³)
6	PETN12	13	1.36
5 7	PETN12	11.4	1.3621
8	PETN16	13.6	1.3576
9	PETN16	11.2	1.3596
CT23	PETN84	13.8	1.3486
10 CT24	PETN88	14.1	1.3495
CT25	PETN92	16.2	1.3449
CT26	PETN95	13.2	1.3449
CT27	PEN	12	1.3499

15 CT: indicates Comparative test.

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Claims

1. A film or hollow shaped article prepared from a low PETN copolymer resin wherein the resin has an oxygen permeability of less than 2000 cc- $\mu\text{m}/\text{m}^2\text{-day-atmos}$ at 30°C.
- 5 2. A film or hollow shaped article prepared from a low PETN copolymer resin wherein the film or the walls of the article comprise a resin which has a density of greater than 1.3400 g/cm³, preferably greater than 1.3500 g/cm³.
3. A film or hollow shaped article prepared from a low PETN copolymer resin wherein the film or the walls of the article comprise a resin in which the area of the peak
10 in $\tan \delta$ centred at $T\beta$ is less than 75% of that for PET.
4. A film or hollow shaped article as claimed in any of Claims 1 - 3 wherein the low PETN copolymer resin is in the range PETN12 to PETN16.
5. A film or hollow shaped article as claimed in Claim 4 wherein the low PETN copolymer resin is PETN12 or PETN16.
- 15 6. A hollow shaped article as claimed in any of Claims 1 - 5 in the form of a container or bottle.
7. A process for the preparation of a film as claimed in any of Claims 1 - 5 which process comprises the step of biaxially drawing a sheet of low PETN copolymer resin under tension to a draw ratio of at least 11.
- 20 8. A process for the preparation of a film as claimed in Claim 7 wherein the draw ratio is between 11 and 15.
9. A process for the preparation of a film as claimed in Claim 7 wherein the low PETN copolymer resin is drawn at a temperature between $T_a + 15^\circ\text{C}$ and $T_a + 30^\circ\text{C}$ thereof.
- 25 10. A process for the preparation of a film as claimed in Claim 7 wherein the low PETN copolymer resin is drawn at a rate of at least 425% strain/sec.
11. A process for the preparation of a film as claimed in any of Claims 7-10 which process comprises the step of casting the sheet of low PETN copolymer from the melt.
12. A process for the preparation of a hollow shaped article as claimed in any of
30 Claims 1 - 6 which process comprises the Steps of:
A) forming a preform by injection moulding a low PETN copolymer resin; and
B) biaxially stretching the preform by blowing to a blow-up ratio of at least 11.

13. A process for the preparation of a hollow shaped article as claimed in Claim 12 wherein the blow-up ratio is between 11 and 15.

14. A process for the preparation of a hollow shaped article as claimed in Claim 12 or 13 wherein the biaxial stretching in Step B is carried out at a temperature between

5 $T_{\alpha}+15^{\circ}\text{C}$ and $T_{\alpha}+30^{\circ}\text{C}$ of the low PETN copolymer resin.

15. A process for the preparation of a hollow shaped article as claimed in any of Claims 12 - 14 wherein the biaxial stretching in Step B is carried out at a draw rate of at least 425% strain/sec.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/00610

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C49/00 B29C55/00 //B29K67:00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C C08G C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 415 728 A (MITSUI PETROCHEMICAL IND) 6 March 1991 see page 7, line 30 - line 34; examples 1-4; table 1 ---	1-15
A	US 4 535 025 A (JABARIN SALEH A) 13 August 1985 see table 1 ---	1
A	US 5 213 856 A (PO' RICCARDO ET AL) 25 May 1993 see claim 1; table -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

30 May 1997

Date of mailing of the international search report

09.06.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Attalla, G

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information on patent family members

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